

# Studies on Hydrogen Sensing by Anodized Nanoporous Titania Thin Film Using Soft Drink Electrolyte

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## Abstract

Nano-porous titanium dioxide (TiO<sub>2</sub>) thin films were developed by UV assisted potentiostatic anodization of 99.7% pure titanium foil. The internationally popular soft drink 'Coca-Cola' was used as the electrolyte in this anodization process. Electrochemical oxidation and photoetching were carried out at room temperature and at 10 V potentiostatic bias without and with 400 W UV light illumination respectively. The prepared TiO<sub>2</sub> thin film was annealed at 150°C for 3 hours. The surface of the prepared TiO<sub>2</sub> film was characterized with Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) to confirm the crystallinity, porous structure and surface roughness. The Optical study revealed a band gap of 3.898 eV. Hot probe method exhibited n-type conductivity of the electrochemically grown TiO<sub>2</sub> thin films. Palladium-Silver alloy (Pd-Ag) contacts were deposited laterally on the oxide surface as catalytic metal electrodes to fabricate a planar sensor configuration. The hydrogen sensor study was carried out at different temperatures (100 to 200°C) and in different hydrogen gas concentrations (1000 to 10000 ppm). Nanocrystalline and nano-porous TiO<sub>2</sub> sensor was promising to sense hydrogen in air ambient with relatively fast response and recovery times (e.g. ~2.9 s and ~75 s) at the optimum temperature of 150°C. Brief mechanism behind the sensing performance has been also discussed.

## Keywords

Electrochemical Oxidation; Coca-Cola Electrolyte; Titanium Dioxide; Nano-Porous TiO<sub>2</sub>; Hydrogen Sensor; Fast Response.

## Introduction

Titanium dioxide thin film is widely investigated for

different applications because of its excellent temperature stability and interesting chemical, electrical and optical properties [Alessandri et al., 2007, Lee et al., 2008]. TiO<sub>2</sub> thin film is also a popular gas sensing material because of its very good chemical stability at high temperature and harsh environment [Pakma et al., 2008]. Various methods have been used to prepare TiO<sub>2</sub> thin films like DC reactive magnetron sputtering, electron beam deposition, atomic layer deposition, thermal oxidation, electrochemical anodization, plasma enhanced chemical vapor deposition (PECVD) and sol-gel technique [Pakma et al., 2008, Bengi et al., 2010]. Electrochemical anodization is one of the most popular techniques for the preparation of porous and tube like TiO<sub>2</sub> thin film structures. Different types of electrolytes like HF, H<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>F, H<sub>3</sub>PO<sub>4</sub> [Paulose et al., 2006, Shimizu et al., 2002, Zhu et al., 2008] are reported for the anodization of TiO<sub>2</sub> thin film. The porous TiO<sub>2</sub> thin film is known to increase the interaction of sensing gas molecules with the oxide surface due to much higher surface to volume ratio leading to higher gas sensitivity at relatively low temperature and low concentration of test gases [Hazra et al., 2006]. Very stable, reproducible and consistent sensing performance were observed at low temperature.

Hazra and Basu reported on the preparation of Al doped titania by thermal oxidation of high purity Ti at 800°C and the development of porous structure by UV assisted electrochemical etching using dilute

H<sub>2</sub>SO<sub>4</sub> electrolyte. Shimizu et al reported H<sub>2</sub> sensing by anodically grown TiO<sub>2</sub> thin film with controlled porous morphology by using different electrolytes (e.g. Aqueous solutions of H<sub>2</sub>SO<sub>4</sub> and NaOH) and different oxidation temperatures. In the present work Coca-Cola, one of the most popular soft-drinks throughout the world, which contains different possible ingredients like phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), Caffeine (C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>), citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>), fructose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>), carbon dioxide, sugar and water, was used as an electrolyte to prepare TiO<sub>2</sub> thin film by electrochemical anodization and UV assisted photoetching. Coca-Cola is acidic and has the pH value of ~2.6 mainly due to the presence of phosphoric acid. The advantage of using Coca-Cola as the electrolyte is more controlled anodization due to relatively weak electrolyte strength and slow photoetching. The anodization process was followed by photoetching using the exposure of UV light to create a nano-porous oxide surface by electrochemical dissolution of titanium dioxide. This nano-porous TiO<sub>2</sub> thin film was subsequently used for hydrogen sensing. Detailed morphological study was done by SEM and AFM to calculate the pore dimension, the particle dimension and the roughness of the titania layer. Planar resistive device structure was fabricated for sensor study using Palladium-Silver alloy (Pd-Ag) contact as the catalytic electrode metal. Hydrogen sensor study showed consistent and reliable performance with 12.1% response, 2.9 s response time and 75.9 s recovery time using 10000 ppm H<sub>2</sub> in air at the operating temperature of 150°C.

## Experimental

### Electrochemical Deposition and UV Assisted Etching

High purity titanium (99.7%) foil (0.25 mm thick) from M/S Sigma Aldrich, USA was used as the starting material for the growth of titanium dioxide thin film. A 14 mm × 14 mm sample was cut and thoroughly washed in an ultrasonic bath using acetone, methanol and deionized water. The electrochemical anodization was carried out in a quartz cell with three electrode configurations of titanium anode, platinum cathode and a Ag/AgCl reference electrode (Fig. 1).

The electrochemical deposition of TiO<sub>2</sub> thin film was carried out using commercial Coca Cola solution as the electrolyte. Three Coca Cola bottles were purchased from three different stores and pH of the Coca Cola solution was measured separately for the

three bottles. The PH value was obtained in the range 2.5 - 2.7. A constant 10 V potential was applied by using scanning potentiostat (PAR Model 362) between the cathode and the anode.

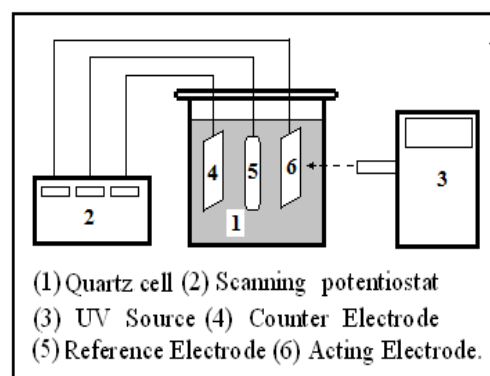


FIG. 1 SCHEMATIC DIAGRAM OF THE ANODIZATION SET UP WITH UV RADIATION SOURCE

The electrode reactions in combination with field driven ion diffusion lead to the formation of an oxide layer on the anode surface. After deposition of the oxide layer that took about one hour, photo electrochemical etching at the same potentiostatic bias was started using 400 watt UV radiation from a fiber optic wave-guide coupled UV source (Model UV-LQ 400, Dr. Gröbel UV-Elektronik GmbH, Germany). The oxide surface was partially etched out by illuminating with UV radiation for 20 min. After etching, the sample was washed with deionized water and dried. Prepared TiO<sub>2</sub> thin film was annealed at 150°C for 3 hours.

### Material Characterizations

The grown TiO<sub>2</sub> thin film was characterized after annealing at 150°C for 3 hours. Crystallinity of the prepared film was confirmed by 2D x-ray diffraction (XRD) technique. The surface morphology of the Titanium Dioxide film was studied by Scanning Electron Microscopy (SEM) (Model: JEOL JSM-6390LV). Atomic Force Microscopy (AFM) (Model: NanoScope IIIa, Digital Instruments) employed to determine the surface roughness, particle diameter and pore dimension using SPIP 6.01.13 AFM imaging tool. Optical band gap of the TiO<sub>2</sub> thin film was evaluated by UV-Visible-NIR optical spectroscopy (Perkin Elmer Lambda-750).

### Schematic of gas sensor structure and electrical contact formation

A 3D view of the planar device is shown in Fig. 2. A 3 mm × 7 mm device with 2 mm separation between two

Pd-Ag alloy contact pads were fabricated for sensor study. Palladium-silver alloy (Pd: 85% and Ag: 15%) with the dimension 2 mm x 2 mm x 0.2  $\mu$ m was deposited on the top surface of the titanium oxide (thickness 2  $\mu$ m) by e-beam evaporation using an Al metal mask. The electrical connections were made by using fine copper wire attached to the pads using silver paste.

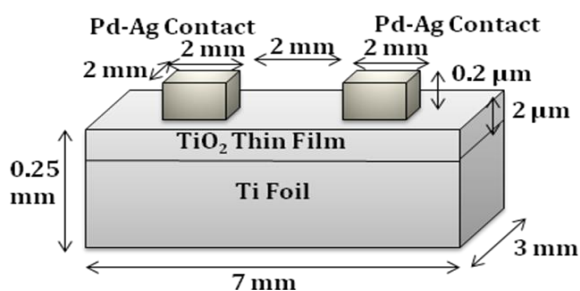


FIG. 2 THE SCHEMATIC OF THE PLANAR GAS SENSOR DEVICE (NOT TO SCALE).

### Gas Sensor Set Up

The sensor set up consists of stainless steel tube gas transmission lines fitted with mass flow controllers and mass flow meters (Digiflow, USA), a closed corning glass tube with inlet and outlet provisions for gases and placed co-axially inside a resistively heated furnace with a 4 cm constant temperature zone and a precise temperature controller ( $\pm 1^\circ\text{C}$ ) with a built-in copper constantan thermocouple [Kanungo et al., 2009]. A computer interfaced Agilent digital multimeter (Agilent U1252A) was employed for the data acquisition. High purity hydrogen and air were used for the experiments. The sensing experiments were repeated using three identically prepared sensor devices and a variation of  $\sim 2\%$  in reading was observed.

## Results and Discussions

### Synthesis of Nanocrystalline Titania Thin Film

Coca-Cola is a soft drink with an acidic nature (pH  $\sim 2.6$ ) mainly due to the presence of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) which is a good but weak electrolyte for porous  $\text{TiO}_2$  thin film preparation [Paulose et al., 2006, Park et al., 2010, Ishikawa et al., 2002]. The thickness of anodically grown oxide depends mainly on the nature of the electrolyte and the applied potential [Jackson et al., 2007]. This experiment was done in the potentiostatic mode with constant voltage of 10 V. Current through Coca-Cola electrolyte was recorded continuously and the current vs time curve was

plotted as shown in Fig 3. The current decreased slowly from 1.28 mA to 0.34 mA and then saturated after 60 min in the dim light laboratory environment that referred to as dark in the manuscript.

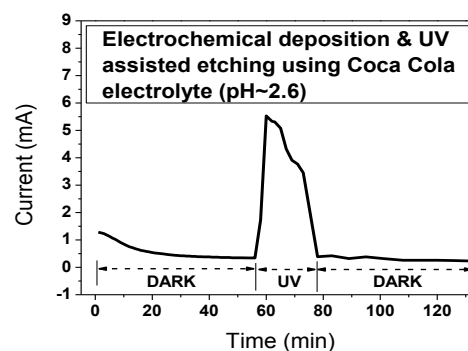
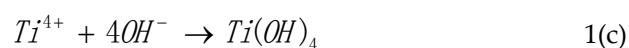
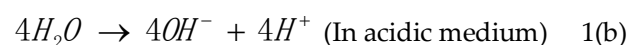


FIG. 3 CURRENT VS TIME CHARACTERISTICS AT CONSTANT POTENTIAL OF 10 V DURING THE ANODIZATION PROCESS.

After the application of 10 V constant potential, the titania layer started to grow and was slowly transformed to a dense layer when the current through the electrolyte became saturated. Since  $\text{TiO}_2$  has higher resistivity than the electrolyte, the applied voltage would make a potential drop over the oxide film on the anode [Jackson et al., 2007]. As long as the electrical field was strong enough to drive the ion conduction through the oxide, the oxide film would keep growing as shown in Fig. 4a. The reactions corresponding to the oxide layer deposition are as follows [Hazra et al., 2006, Ishikawa et al., 2002]:



When the applied potential crossed the dielectric breakdown limit of the grown  $\text{TiO}_2$  layer, pores were created at the weak point of the oxide layer [Choi et al., 2004]. Ti exposed through the pores in contact with the electrolyte and more oxide layers formed following Eq. 1 were shown in Fig. 4b and 4c. Electrochemical oxidation is a combined process of oxide formation and oxide dissolution in the electrolyte [Sugiura et al., 1998]. The creation of pores in the oxide layer also depends on the dissolution rate of the deposited oxide on the Ti substrate [Choi et al., 2004].

In this experiment, 400 watt UV radiation was applied for 20 min to activate the surface locally to generate excess number of pores on the oxide surface by electrochemical etching as indicated by the increase of

current (Fig. 3). The electrochemical etching process upon UV illumination is due to the generation of excess holes & electrons in the valance band followed by the excitation of electrons to the conduction band of the active oxide insulator [Hazra et al., 2006]. These generated charge carriers enhance the ionic conduction through the electrolyte and increase the oxide etching rate under a constant potentiostatic bias, thereby producing the porous structure.

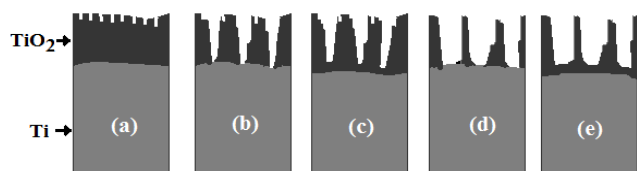


FIG. 4 POROUS  $\text{TiO}_2$  THIN FILM FORMATION IN THE DARK AND ON UV ILLUMINATION USING COCA-COLA AS THE ELECTROLYTE (a) OXIDE GROWTH IN THE DARK (b) PORE FORMATION DUE TO DIELECTRIC BREAKDOWN AND EXPOSURE OF Ti (c) FURTHER  $\text{TiO}_2$  GROWTH INSIDE THE PORE IN THE DARK (d) EXCESS PORE FORMATION ON UV ILLUMINATION AND (e) GROWTH OF MORE  $\text{TiO}_2$  LAYER ON THE Ti EXPOSED AREA IN THE DARK ENVIRONMENT.

The Oxide was partially dissolved in the electrolytic solution on UV exposure and pores were generated on the oxide surface as shown in Fig. 4d [Choi et al., 2004]. Subsequently, the residual titanium surface exposed at the bottom of the pores got oxidized to form insulating layer. For this reason the current initially increased upon UV exposure because of etching of the oxide and then gradually decreased due to formation of more oxide on removal of UV illumination. Finally the current tended to saturate. Fig. 4e shows that all the Ti exposed in the pores was oxidized in the dark environment.

#### Characterization of Nano-porous $\text{TiO}_2$ Thin Film

The 2D-XRD model D/max-RAPID Rigaku micro-diffractometer was used to study the x-Ray diffraction of the grown titania thin film was identified as anatase nanocrystalline structure [He et al., 2009].

Scanning Electron Micrograph (SEM) of UV assisted electrochemically grown  $\text{TiO}_2$  thin film using Coca-Cola electrolyte is shown in Fig. 5 which represents the porous nature of the  $\text{TiO}_2$  film surface. Most of the pores are oval in shape with the longitudinal appearance.  $\text{TiO}_2$  thin film surface was heavily etched due to UV exposure which is clearly shown in the

SEM image (Fig. 5).

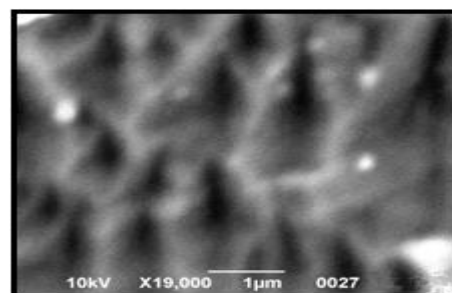


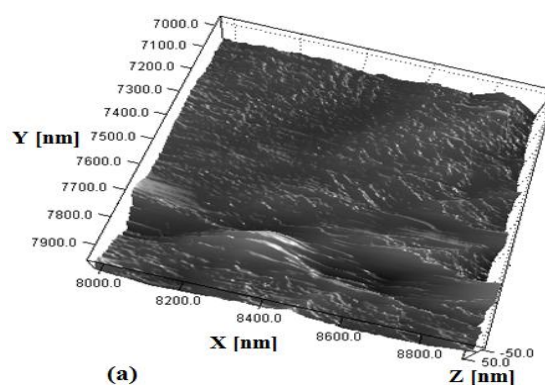
FIG. 5 SEM IMAGE OF ANODICALLY GROWN POROUS  $\text{TiO}_2$  THIN FILM USING COCA-COLA AS AN ELECTROLYTE.

The surface roughness of UV assisted anodically grown  $\text{TiO}_2$  thin film was measured by AFM. The sample was scanned over  $1000 \text{ nm} \times 1000 \text{ nm}$  area and the AFM images with 3D and 2D topography are shown in Fig.6. Root mean square roughness ( $R_q$ ) is 16.5 nm and the difference between the lowest and highest points on the surface ( $R_{p-p}$ ) is 100 nm. Different types of surface roughness values have been calculated from the AFM and plotted in Fig. 7.

The Pore size and the particle size were also calculated from the AFM analysis and presented in Table 1. An average pore diameter of 16.69 nm was calculated indicating the nano-porous structure of the anodically grown  $\text{TiO}_2$  thin film and an average particle diameter of 15.57 nm was obtained. Nano-porous structure of the  $\text{TiO}_2$  thin film is also clearly shown in the 3D presentation of the AFM image.

TABLE 1 PARTICLE AND PORE DIAMETER OF  $\text{TiO}_2$  THIN FILM CALCULATED FROM AFM ANALYSIS

Dimension	Particle Diameter (nm)	Pore Diameter (nm)
Maximum	247.45	167.55
Minimum	1.48	1.71
Average	15.57	16.69



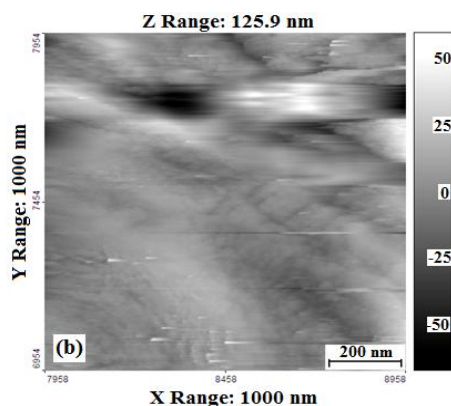


FIG. 6 AFM IMAGE OF ANODICALLY GROWN POROUS  $\text{TiO}_2$  THIN FILM USING COCA-COLA AS THE ELECTROLYTE (a) 3D TOPOGRAPHY (b) 2D TOPOGRAPHY

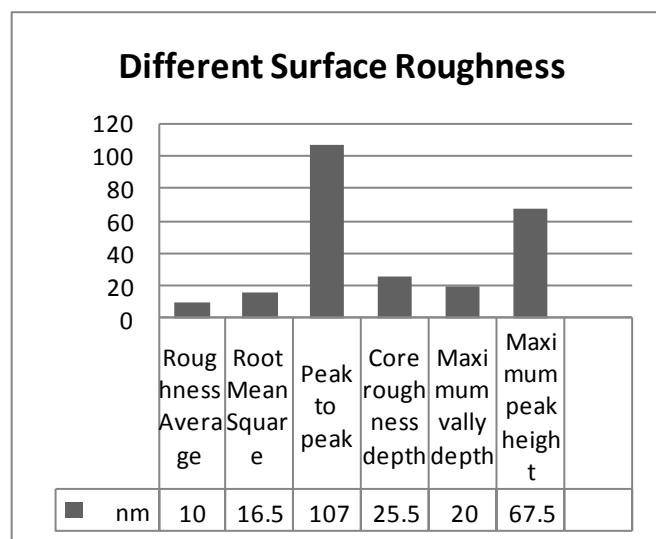


FIG.7 SURFACE ROUGHNESS CHART OF ANODICALLY GROWN POROUS  $\text{TiO}_2$  THIN FILM USING COCA-COLA AS THE ELECTROLYTE AS OBTAINED FROM THE AFM IMAGE.

The optical band gap of the electrochemically grown nano-porous  $\text{TiO}_2$  thin film was determined by the reflection spectrum shown in Fig. 8a. The absorption coefficient,  $\alpha$  and the optical band gap,  $E_g$  of the material were related to the Tauc relation in Eq. 2.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where, ' $E_g$ ' the optical energy gap, ' $A$ ' is a constant, and the index ' $n$ ' can have values  $1/2$ ,  $3/2$ ,  $2$ , and  $3$ , depending on the nature of the electronic transition responsible for reflection. From the UV-VIS-NIR spectroscopy, the reflection spectrum was obtained and an optical band gap ( $E_g$ ) of 3.898 eV for the UV assisted anodically grown nano-porous  $\text{TiO}_2$  thin film using Coca-Cola electrolyte was calculated. The higher value of the calculated  $E_g$  compared to that of the single crystal/ polycrystalline Titania ( $E_g \sim 3.36$  eV) further indicated the nano crystalline nature of the grown Titania thin film in the present study.

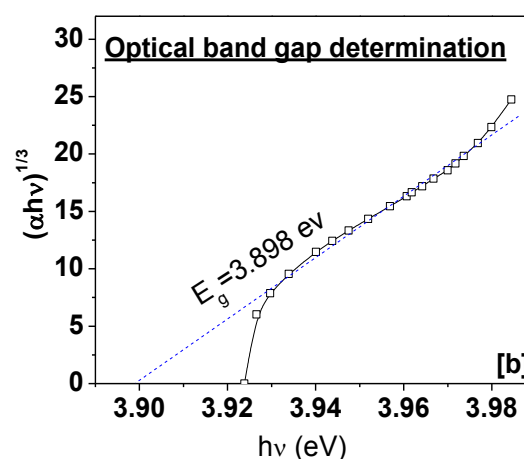
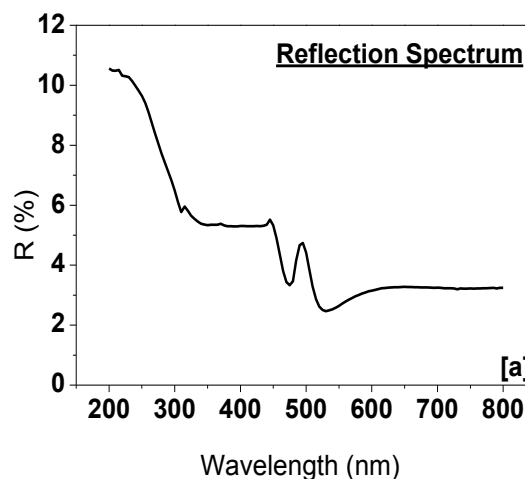


FIG.8 OPTICAL STUDY OF  $\text{TiO}_2$  THIN FILM GROWN ELECTROCHEMICALLY IN COCA-COLA SOLUTION (a) REFLECTION SPECTRA AND (b) OPTICAL BAND GAP DETERMINATION.

The type of semiconductivity of the electrochemically grown  $\text{TiO}_2$  thin film was determined by the well known hot probe method and it was found to be n-type. A multimeter was attached to the sample, and a heat source (like soldering iron), was used to heat one terminal. The thermal energy caused charge carriers (electrons) to move away from the heated lead, which generated a voltage difference and the sign of the voltage determined the type of conductivity. The n-type conductivity was additionally confirmed by the reduction of the resistance of Pd-Ag/ $\text{TiO}_2$  sensor device in presence of hydrogen gas.

### Hydrogen Sensing

Hydrogen sensing properties were studied by measuring the change in the electrical resistance of the



sensor with different hydrogen concentrations in the range 1000-10000 ppm mixed with air as carrier gas and in the temperature range 75-200°C. The magnitude of the gas response ( $S$ ) defined here as the ratio of the change in resistance in presence of hydrogen mixed with air ( $R_a-R_g$ ) to the initial resistance in air ( $R_a$ ) at the constant voltage is expressed as

$$S = \left( \frac{R_a - R_g}{R_a} \right) V \quad (3)$$

where  $R_a$  is the resistance in air and  $R_g$  is the resistance in presence of hydrogen mixed with air. The response time of the sensor was calculated as the time taken by the sensor signal to reach 90% of its saturation value upon exposure to hydrogen mixed with air, and recovery time was calculated as the time corresponding to the decrease of the sensor signal by 90% of its saturation value after the hydrogen was cut off. [Hazra et al., 2006, Kanungo et al., 2009].

Fig. 9(a) & Fig. 9(b) present the response magnitude vs temperature and the response time and recovery time vs temperature respectively of the anodically grown  $\text{TiO}_2$  based planar sensor device in the temperature range, 75-200°C. While the response is quite slow at low temperature region, a serious base line fluctuation [Fig.10] was observed during the repeated cycle measurements above 150°C. So, considering the viable sensing operation from the point of view of reproducibility and stability, it was depicted from our experiments that 150°C should be the optimum temperature for the  $\text{TiO}_2$  based sensor devices fabricated in the present investigation using the electrochemical method.

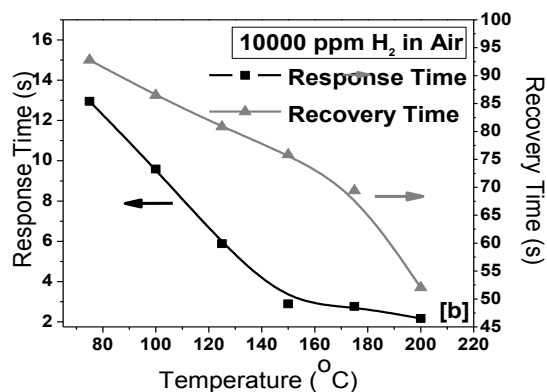
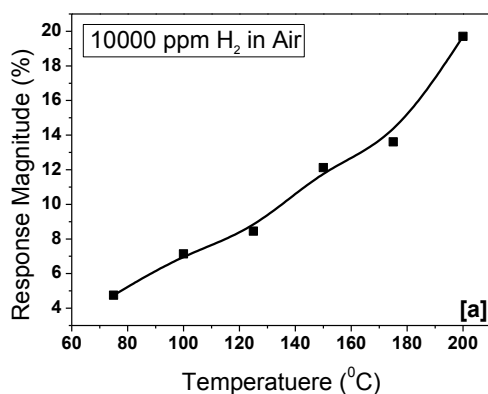


FIG. 9 (a) RESPONSE MAGNITUDE VS. TEMPERATURE CHARACTERISTICS (b) VARIATION OF RESPONSE TIME AND RECOVERY TIME WITH TEMPERATURE OF THE  $\text{TiO}_2$  PLANAR SENSOR.

Fig. 10 represents the repeated cycle response plot in 10000 ppm hydrogen in air at 100°C, 150°C and 200°C for the  $\text{TiO}_2$  based planar sensor devices. The figures show the best repeatability at 150°C with optimum response and stable base line.

In the temperature range, 75-200°C, the response magnitude was shown increasing [Fig. 9(a)] and the response time and recovery time decreased [Fig. 9(b)] with the increasing temperature. Table 2 presents the numerical data over the entire sensing temperature range. Although both Fig. 9 and Table 2 show that the sensor performance improves with increasing temperature, it was observed that the sensor device deteriorates at higher temperature and it is evident from the lack of reproducibility and base line shift (Fig.10) which is in good agreement with the adsorption and desorption kinetics of gases on the solid. There is an optimum temperature of adsorption and the reaction kinetics is decelerated with the on-set of desorption that usually occurs at elevated temperatures. Hydrogen trapped in the nano-crystalline oxide surface lattice gets desorbed much faster at higher temperatures and is removed by the reaction with air in the surrounding. Therefore, the recovery time becomes faster while the decrease in response time is relatively slow at higher temperatures due to decrease in the adsorption rate. Fig. 10 demonstrates that, in the temperature range of 75-150°C, sensor showed stable and repeatable performance without any base line fluctuation but the sensor response was significantly low. On the other hand, in the temperature range 150-200°C, the sensor response was appreciably high but there was fluctuations in the base line. So, 150°C was regarded as

the optimum temperature with the response magnitude of 12.1%, response time of 2.9 s and recovery time of 75.9 s.

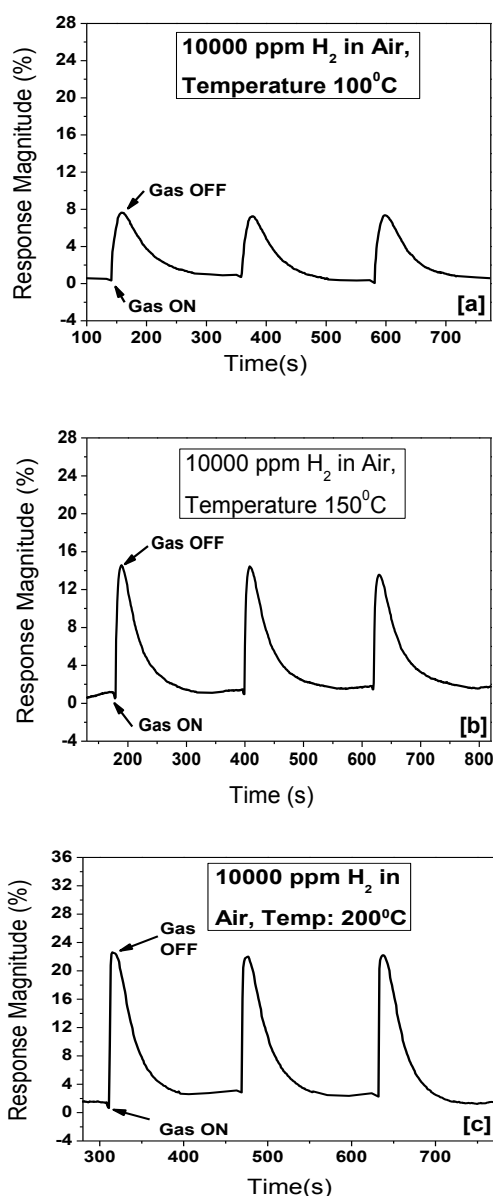


FIG. 10 REPEATED CYCLE RESPONSE FOR THE SENSOR SAMPLE AT (a) 100°C, (b) 150°C AND (c) 200°C

TABLE 2 RESPONSE, RESPONSE TIME AND RECOVERY TIME OF THE ELECTROCHEMICALLY GROWN  $\text{TiO}_2$  SENSORS IN THE TEMPERATURE RANGE OF 75-200°C IN PRESENCE OF 10000 PPM  $\text{H}_2$  BALANCED WITH AIR.

Temperature (°C)	Response Magnitude (%)	Response Time (s)	Recovery Time (s)
75	4.75	12.9	92.8
100	7.14	9.6	86.5
125	8.45	5.9	80.8
150	12.12	2.9	75.9
175	13.61	2.8	69.4
200	19.71	2.2	52.0

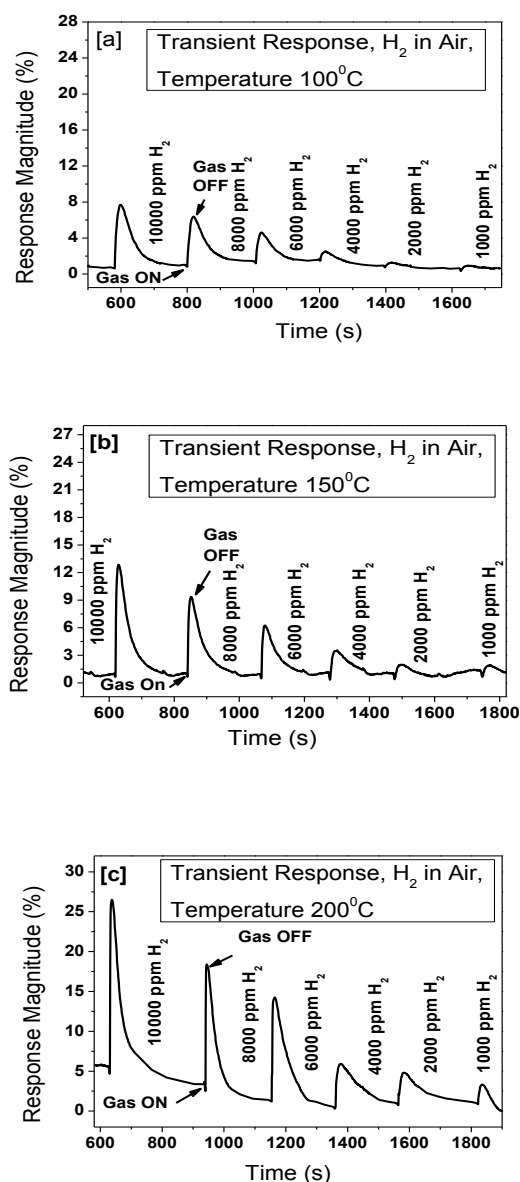


FIG. 11 RESPONSE TRANSIENT WITH DIFFERENT CONCENTRATIONS OF  $\text{H}_2$  (1000-10000 PPM) IN AIR AS CARRIER GAS AT (a) 100°C (b) 150°C (c) 175°C.

Fig. 11 presents the sensor response of electrochemically grown  $\text{TiO}_2$  sensor upon interaction with  $\text{H}_2$  as a function of time at three different temperatures e.g. 100, 150 and 200°C. Systematic decrease of sensor response with decreasing hydrogen concentration is clearly apparent from the transient response curves. At 100 and 150°C, there is no base line fluctuation observed in the transient response curve [Fig.11(a-b)] where as a serious base line fluctuation is clearly observed in [Fig.11(c)] at 200°C. This further supports our arguments in favor of choosing 150°C for studying the hydrogen sensing properties of Pd-Ag/ $\text{TiO}_2$  resistive

sensor devices.

### **Sensing Mechanism**

According to the space charge layer model, oxygen is adsorbed from the ambient to the oxide surface at certain temperature [Akbar et al., 1997]. The adsorbed oxygen extracts electrons from the film surface and forms the depletion region near the grain boundary. For sensing hydrogen when  $\text{TiO}_2$  thin film is exposed to the hydrogen gas, electrons are injected back to the surface. So, the number of electrons increases at the conduction band thereby increasing the conductivity of the oxide. The change of the resistance of  $\text{TiO}_2$  thin film is measured in presence of hydrogen gas [Lu et al., 2009, Zakrzewska et al., 2004]. This is, of course, the most popular and basic gas sensing mechanism to detect reducing gases by metal-oxide gas sensors.

Electrochemically grown porous  $\text{TiO}_2$  thin film surface with a large area due to vertically aligned nano pores of  $\sim 16$  nm diameter adsorbed a large volume of oxygen species [Lee et al., 2011] that interacted with  $\text{H}_2$  molecules which diffused efficiently through the vertically aligned  $\text{TiO}_2$  nano-pores. Therefore, the anodically grown  $\text{TiO}_2$  based hydrogen sensor detected 10000 ppm  $\text{H}_2$  quite efficiently at relatively low temperature of  $150^\circ\text{C}$  with a response time of  $\sim 2.9$  s and a recovery time of  $\sim 75$  s. However, the percentage gas response shows quite a low value ( $\sim 12\%$ ), but it is simple to amplify the sensor response by standard electronic devices for the practical applications. It should be mentioned here that hydrogen makes an explosive mixture with air/oxygen between 4% and 76%. Therefore, hydrogen sensor with detectability of 1% can be considered useful for commercial purposes.

Palladium (Pd) is widely known catalytic metal used as electrode in the hydrogen detector because of its well known hydrogen adsorbing quality. But when it adsorbes large quantity of hydrogen, palladium can chemically interact with hydrogen to form two non-stoichiometric hydride phases, namely,  $\alpha$  ( $\sim \text{PdH} < 0.03$ ) and  $\beta$  ( $\sim \text{PdH} < 0.83$ ) [Hüberta et al., 2011].

For the sensing purpose, continuous hydrogen adsorption and desorption on the Pd surface may induce a weakening effect of the metal structure and can cause cracking and/or blistering of the metal films [Amandusson et al., 2001]. Since alloying Pd with Ag (12% to 33%) can prevent the hydride formation, Pd-

Ag alloy (Pd: 85% and Ag: 15%) was used as the electrode material in the present study. Apart from decreased hydrogen diffusivity, Pd-Ag alloy has higher mechanical strength than pure Pd which becomes fragile after certain number of cycles due to transformation to  $\beta$  hydride phase [Hüberta et al., 2011, Amandusson et al., 2001]. Pd-Ag lattice is less influenced by hydrogen and thus it is less brittle than the pure Pd lattice because the lattice has already been expanded by the silver atoms [Bohmholdt et al., 1967].

Iwanaga et al reported that the pure Pd electrode becomes partially oxidized during prolonged air treatment [Iwanaga et al., 2003]. In the present work, the sensor study was performed in air used as the carrier gas. So, there was a strong possibility of PdO formation at the optimum sensing temperature of  $150^\circ\text{C}$ . When the sensor device was exposed to  $\text{H}_2$ , PdO was reduced to Pd and the work function of the metal increased [Shimizu et al., 2007]. Therefore, the barrier height of the metal-semiconductor junction also increased leading to increased junction resistance. Simultaneously,  $\text{H}_2$  gas molecules might be dissociated to hydrogen atoms on the Pd surface and got dissolved into the Pd bulk. Work function of Pd decreased due to dissolution of H atom in the Pd bulk [Iwanaga et al., 2003]. As a result, the barrier height at the metal-semiconductor interface decreased and the junction resistance also decreased. Thus, the two competitive reactions e.g. PdO to Pd formation and  $\text{H}_2$  dissociation to H atoms followed by dissolution in Pd might be the possible reasons of the complications in the sensing mechanism.

### **Conclusions**

The present study of sensing hydrogen in air using Titanium dioxide thin film grown by electrochemical anodization and photoetching in the Coca-Cola electrolyte is quite interesting from the point of novel approach of using a commercial soft drink as electrolyte to make an oxide thin film that may develop an efficient gas sensor. The advantage of using this weak electrolyte is to better control the thin film growth due to slower oxidation rate compared to the stronger inorganic acid electrolytes normally used to produce nano crystalline oxide thin films by anodization method. The photoetching can also be better regulated by reducing the effect of UV light passing through the coloured electrolyte. In fact, this study can suggest to use some dye material in the



electrolyte during electrochemical oxidation and photo etching to produce nano porosity that are mostly confined near the surface.

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#### REFERENCES

- Alessandri, I., E. Comini, E. Bontempi, G. Faglia, L. E. Depero, G. Sberveglieri, "Cr-inserted TiO<sub>2</sub> thin films for chemical gas sensors", *Sens. Actuators B* 128 (2007) 312–319.
- Amandusson, H., L.-G. Ekedahl, H. Dannelun, "Hydrogen permeation through surface modified Pd and PdAg membranes", *J. Membrane Science* 193 (2001) 35–47
- Akbar S. A., L. B. Younkman, "Sensing Mechanism of a carbon monoxide sensor based on anatase titania" *J. Electrochem. Soc.*, 144 (1997) 1750–53
- Bengi, A., U. Aydemir, S. Altındal, Y. Özen, S. Özcelik, "A comparative study on the electrical characteristics of Au/n-Si structures with anatase and rutile phase TiO<sub>2</sub> interfacial insulator layer", *J. Alloys and Compounds* 505 (2010) 628–633.
- Bohmholdt, G., E. Wicke, "Zur diffusion von wasserstoff und deuterium in palladium und Pd-Legierungen", *Z. Phys. Chem. Neue Folge* 56 (1967) 133
- Choi, J., R. B. Wehrspohn, Jaeyoung Lee, Ulrich Gösele, "Anodization of nanoimprinted titanium: a comparison with formation of porous alumina", *Electrochimica Acta* 49 (2004) 2645–2652.
- Hazra, S.K., S. Basu, High sensitivity and fast response hydrogen sensors based on electrochemically etched porous titania thin films, *Sens. Actuators B* 115 (2006) 403–411.
- He, B. Bob, "Two-Dimensional X-Ray Diffraction", John Wiley & Sons, Inc., Hoboken, New Jersey 2009
- Hüberta, T., L. Boon-Brett, G. Black, U. Banach, "Hydrogen sensors – A review", *Sensors and Actuators B* 157 (2011) 329–352
- Ishikawa, Y., Y. Matsumoto, "Electrodeposition of TiO<sub>2</sub> photocatalyst into porous alumite prepared in phosphoric acid", *Solid State Ionics* 151 (2002) 213–218
- Iwanaga, T., T. Hyodo, Y. Shimizu, M. Egashira, "H<sub>2</sub> sensing properties and mechanism of anodically oxidized TiO<sub>2</sub> film contacted with Pd electrode", *Sens. Actuators B* 93 (2003) 519–525
- Jackson, M.K., W. Ahmed, "Surface Engineered Surgical tools and Medical Device", Springer Science, 2007.
- Kanungo, J., H. Saha, S. Basu, "Room temperature metal–insulator–semiconductor (MIS) hydrogen sensors based on chemically surface modified porous silicon", *Sens. Actuators B* 140 (2009) 65–72
- Lee, J., D. H. Kim, S.-H. Hong, J.Y. Jho, "A hydrogen gas sensor employing vertically aligned TiO<sub>2</sub> nanotube arrays prepared by template-assisted method", *Sensors and Actuators B* 160 (2011) 1494–1498
- Lee, H., S. A. Akbar, "Sensing behavior of TiO<sub>2</sub> thin-film prepared by rf reactive sputtering," *Sensors Letter*, 6 (2008) 1049–1053.
- Lu, C., Z. Chen, "High-temperature resistive hydrogen sensor based on thin nanoporous rutile TiO<sub>2</sub> film on anodic aluminum oxide", *Sens. Actuators B* 140 (2009) 109–115
- Pakma, O., N. Serin, T. Serin, Ş. Altındal, "The double Gaussian distribution of barrier heights in Al/TiO<sub>2</sub>/p-Si (metal-insulator-semiconductor) structures at low temperatures", *J. App. Phys.* 104, (2008) 014501.
- Park, J.-W., Y.-J. Kim, J.-H. Jang, T.-G. Kwon, Y.-C. Bae, J.-Y. Suh, "Effects of phosphoric acid treatment of titanium surfaces on surface properties, osteoblast response and removal of torque forces", *Acta Biomaterialia* 6 (2010) 1661–1670
- Paulose, M., K. Shankar, S. Yoriya, H. E. Prakasam, O. K. Varghese, G. K. Mor, T. A. Latempa, A. Fitzgerald and C. A. Grimes, "Anodic Growth of Highly Ordered TiO<sub>2</sub> Nanotube Arrays to 134 µm in Length", *J. Phys. Chem. B*, Vol. 110, No. 33 (2006) 16179–16184.
- Shimizu, Y., N. Kuwano, T. Hyodo, M. Egashira, High H<sub>2</sub> sensing performance of anodically oxidized TiO<sub>2</sub> film contacted with Pd, *Sens. Actuators B* 83 (2002) 195–201.
- Shimizu, Y., T. Hyodo and M. Egashira, H<sub>2</sub> sensing performance of anodically oxidized TiO<sub>2</sub> thin films

equipped with Pd electrode, *Sens. Actuators B* 121 (2007) 219–230.

Sugiura T., T. Yoshida and H. Minoura, ““Designing a TiO<sub>2</sub> Nano-Honeycomb Structure Using Photoelectrochemical Etching” *Electrochem. Solid-State Lett.* 1 (1998) 175-177.

Zakrzewska, K., “Gas sensing mechanism of TiO<sub>2</sub>-based thin films”, *Vacuum* 74 (2004) 335–338

Zhu, X., J. Chen, L. Scheideler, R. Reichl, J. Geis-Gerstorfer, “Effects of topography and composition of titanium surface oxides on osteoblast responses”, *Biomaterials* 25 (2004) 4087–4103.

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